I. STRUCTURE AND PHYSICAL PROPERTIES OF MASSIVE NYLON

II. SPECTROPHOTOMETRIC EVALUATION OF LUBRICATING OILS

BY

MELVIN HENRY MUELLER

B.A., Iowa State Teachers College, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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I. STRUCTURE AND PHYSICAL PROPERTIES OF MASSIVE NYLON

Introduction

Nylon as a fiber has been of great commercial importance for some time and recently its use in more massive form has come into prominence. The structure and physical properties of the massive form have not been extensively investigated. Accordingly this investigation has been made in order to add to this knowledge and to make a comparison of behavior of the massive nylon with fibers of this material.

Samples And Procedure

Studies were made of massive nylon ranging in size from .011″ strip to 3″ rod. An x-ray investigation was made using the Geiger Spectrometer and film methods. Hardness measurements were made with a Superficial Rockwell and a Tukon Tester. A microscopic study of the polished specimens was made using incident light and density measurements were made with a pyncnometer.

Conclusions And Summary

1. The two principal peaks or rings found in the x-ray pattern of non-oriented nylon have previously been found to arise from the 100 planes and a combination of the 110 and the 010 planes. The latter has the greater 2θ value and consequently represents a smaller spacing than the former. In the present study of the massive nylon as received it was found that the position of the peak from the 100 plane remained relatively constant varying approximately 0.05 A. U. between the two extreme sizes studied. The d spacing found for the larger pieces was approximately 4.40 A. U. and for the thin strip, which is cooled more rapidly from the molten state, approximately 4.35 A. U. This is in good agreement with the value reported by Bunn and Garner (1) and Ecochard (2).

However, there is a considerably greater difference in the position of the other peak, arising from the 010 and 110 planes. In the smallest pieces this peak had a d value of 3.92 A. U. and for the largest the d was 3.76 A. U. A slight difference was also noted in the position of this peak between the inside and outside of some of the rods. This difference in spacing is apparently dependent upon the cooling rate. The faster the cooling rate the greater the value of 2 θ of the 100 reflection and the smaller the value of 2 θ from the 110 and 010 planes. A comparison of the Geiger spectrometer curves obtained from specimens of widely different size showed that the peaks are sharper and better defined as the size increased, indicating a higher degree of crystallinity with slower cooling.

2. Upon heating the thin strip material, such as the .028" strip, in an oil bath up to 235° C. the peak caused by diffraction from the 110 and 010 planes shifted in relation to the other peak and both peaks became sharper at the higher temperatures. Brill (3) had previously noticed that one spacing remained constant when heating nylon fibers. Fuller, Baker and Pape (4) had reported little or no change in position of these lines upon annealing thin films of nylon.

In the present investigation it was found that the amount of shifting taking place is governed by the temperature of the anneal. The higher the temperature the greater the shift and, furthermore, the entire change takes place within a few minutes and additional heating produces no additional effect. Curves were again made of the initially heated .028" strip, after standing at room temperature for six months and found to show the same shift, thus indicating a permanent effect.

In contrast to the shifting observed after heating the .028" strip, the larger pieces exhibited little or no change even at the higher temperatures.

It would seem from the range of differences in 2 θ between the peaks found in the material as received and after heating that a gradual movement of the chains in relation to each other must be possible. This may mean that there is a per-

missible variation in the dimensions of Bunn's α unit cell rather than a change from the β to α form.

3. The effect of heating in various media was determined by heating .028″ strip in oil, water, air and silicone fluid at the same temperature. There was considerable difference in the amount of shifting taking place with the greatest amount after heating in water. The peak from the 100 planes remained constant again and both peaks were the sharpest and best defined after heating in water. Bunn has suggested that there is hydrogen bonding in the 010 plane. Brill believes that water will break the hydrogen bonding. If annealing in water breaks the hydrogen bonds, there should be a change in the spacing for the 100 reflection. This shifting produced by the water seemed to be of a permanent nature.

4. Some slight preferred orientation was observed from x-ray patterns taken on film especially in the case of the rod material which can be accounted for by the method of manufacture. In a few cases, even though a fiber pattern was not obtained, an orientation was indicated since the relative intensity of one ring was much smaller than normally observed. This can be accounted for by an orientation in which the 010 plane becomes parallel to the outside of the bar owing to pressure during fabrication.

5. Brill had found that if an x-ray pattern of nylon fibers were taken at an elevated temperature the two diffraction rings gradually came together and at 160° C. fused into one for nylon 66. In this investigation a similar treatment of thin sections taken from a larger piece produced a shifting of one ring; however, even a temperature of 200° C. was not sufficient to fuse the rings into one. Apparently there is a difference in movement allowed in oriented and non-oriented material at a certain temperature.

6. Hardness readings made on the different sizes of nylon as received by both methods of testing indicated, in general, that the material with the initially closer spacing is softer. Heating the strip nylon caused a considerable increase in

hardness. The final hardness obtained, like the amount of shifting of the peaks, is dependent upon the annealing temperature. Again there is a very good correlation between the lack of a change in the hardness and spacing when heating the larger masses such as the 2″ rod.

Even though the 2 θ difference is just as great after heating the strip at 235° C. as the 2″ rod as received, the hardness of the former upon reaching the maximum 2 θ difference is not so hard. This may be explained by a difference in the amount of the crystalline material present. The increased hardness obtained upon annealing the thinner material was found to be permanent just as is the shifting of the peaks.

7. Upon heating in various media the hardness did not change appreciably when heating at 100° C. in oil, silicone fluid or air, but the material became much softer after heating in water. This change was not permanent and can be explained by a plasticizing effect. A similar change, produced by variations in temperature and humidity, caused day to day variations in hardness. These variations were smaller in the larger, more crystalline masses than in the smaller, more rapidly cooled material.

8. A heat-etching effect brings out the flow of the material which took place during fabrication. This heating also made it possible to observe a "grain-like" structure in the material. After applying the metallurgical polishing technique to the specimens of nylon the "grain" structure became visible, after standing in air for a few minutes, without etching. In general, the smallest "grains" appeared in the thin sections and the outermost portions of specimens of larger sizes and the largest "grains" appeared in the center of the specimens with maximum dimensions. Some of these larger "grains" showed evidence of internal cracks. The size of the "grain" is believed to be the result of the cooling rate. These "grains" are made evident partially by a relief polishing in which the material surrounding the "grains" is polished away more rapidly, which is probably due to a smaller degree of crystallinity and hence

softer material.

Even the small "grain" size exhibited by the rapidly cooled specimens showed no change when heated up to 235° C.

When an x-ray beam was allowed to pass through a single large "grain" the pattern obtained had two rings of quite uniform intensity, indicating practically complete random orientation. Hence these "grains" are probably aggregates of spherulites which is quite different from the grains found in metals.

Recrystallization after cold working was confirmed by x-ray and microscopic methods.

9. A slightly lower density was found for the strip material, which may indicate a slightly greater amount of amorphous material in the more rapidly cooled nylon.

10. Considerable difference in tensile strength and elongation has been noted between different rods of nylon and within the same rod. Thus far sufficient differences in the x-ray pattern, hardness, and micro-structure have not been found to account for this. Perhaps the present theory of the fracture of materials, based on the presence of small cracks, or the presence of impurities, may account for these differences in tensile strength and elongation.

11. This investigation has indicated that a similar separate study therefore is certainly required for each type of polymer. There are some entirely unsuspected structural phenomena in polymers, even as common and apparently well known as nylon, as functions of mass, previous history, heat treatment, aging, cold and hot work, impurities, etc.

On the basis of this information certainly nylon in massive form for gears and a variety of other uses may be used more intelligently and performance more adequately predicted and controlled.

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II. SPECTROPHOTOMETRIC EVALUATION OF LUBRICATING OILS

Introduction

In wartime investigations it was found that the performance of quenching oils for aluminum alloy airplane motor castings could be determined by means of spectrophotometric curves of the oils which could be correlated accurately with residual strain in the castings (1). Increased deterioration, easily detected in the absorption measurements, resulted in increased strain. It was logical to extend this optical testing method to lubricating oils in the hope of simplifying the complex procedure of the standard petroleum tests.

Experimental

Through the co-operation of several oil laboratories it was possible to investigate a number of different oils operating under various conditions. Some of the oils were tested under laboratory conditions by means of an Underwood tester and others were tested under actual operating conditions in automobile and diesel engines. After performing a number of the more familiar and accepted tests of the petroleum laboratories

these samples were then diluted with chloroform and used for a spectrophotometric study.

Conclusions

There is a striking similarity between the graphs of the optical data and those for these familiar tests, indicating a definite relationship between the optical properties and these other chemical and physical data indicating relative amounts of oxidation, polymerization and other deterioration with use under many conditions of temperature and catalyzing materials.

Data from these spectrophotometer curves, obtained from oils at standard dilutions, could be used in a variety of ways. These curves could be compared from the basis of shift of the minimum transmission, the flattening of the curve at this point, or the logarithm of the reciprocal of the minimum transmission could be plotted against time of heating during laboratory or Underwood tests, or against miles or hours of service in engines. These curves could then be compared with corresponding curves made by standard tests such as percent asphaltenes, carbon residues, neutralization number, viscosity, chloroform solubles and insolubles, etc. Thus the spectrophotometric method offers a rapid means of rating lubricating oils in advance of their use and a means of determining whether usual engine failures may be ascribed to the lubricating oil.

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VITA

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He attended the Iowa State Teachers College from 1936 to 1940, graduating with the degree of Bachelor of Arts in August 1940. During the following school year he served as a full time assistant in this institution.

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The author is a member of the American Chemical Society, Sigma Xi, and American Society for Metals.

He is a joint author of the following papers:

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